Chapter 2

Time-Dependent (Current-)Density-Functional Theory

2.1 Introduction

In stationary DFT the Hohenberg-Kohn theorem guarantees that the ground-state density uniquely determines the external potential up to an arbitrary constant. One may wonder if a similar statement can be made for time-dependent densities and potentials. The proof that indeed there is such a statement was given by Runge and Gross and will be presented in section 2.3. It is not just a simple extension of the Hohenberg-Kohn theorem since that relies on the Rayleigh-Ritz variational principle for the energy of which there is no equivalent in the time-dependent case. As we will show the Runge-Gross proof is based directly on the time-dependent Schrödinger equation. The Runge-Gross theorem provides the basis for time-dependent density functional theory (TDDFT). A review of TDDFT can be found in Ref. [37]. An overview of the key concepts of TDDFT is given in Ref. [20].

2.2 Preliminaries

Consider a particle system under the influence of some time-dependent external field. For the moment we will only consider systems in which this time-dependent external field can be described by a time-dependent scalar potential $v(\mathbf{r}, t)$. The time-

dependent Hamiltonian of such a many-particle system is given by

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}, \tag{2.1}$$

where the kinetic energy $\hat{T}$ and the two-particle interaction $\hat{W}$ are defined in Eqs. (1.2) and (1.4). The time-dependent external potential $\hat{V}(t)$ is given by

$$\hat{V}(t) = \int d\mathbf{r} v(\mathbf{r}, t)\hat{\rho}(\mathbf{r}), \tag{2.2}$$

where the density operator $\hat{\rho}(\mathbf{r})$ is defined in Eq. (1.7). The dynamics of this system can be obtained by solving the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle, \tag{2.3}$$

evolving from a fixed initial state $|\Psi(t_0)\rangle = |\Psi_0\rangle$. This initial state is often taken to be the ground state. The time-dependent density $\rho(\mathbf{r}, t)$ is obtained as the expectation value of the density operator with the time-dependent many-particle wave function $|\Psi(t)\rangle$,

$$\rho(\mathbf{r}, t) = \langle\Psi(t)|\hat{\rho}(\mathbf{r})|\Psi(t)\rangle. \tag{2.4}$$

Using the quantum mechanical equation of motion for the expectation value of an arbitrary operator $\hat{A}(t)$,

$$\frac{\partial}{\partial t}\langle\Psi(t)|\hat{A}(t)|\Psi(t)\rangle = \langle\Psi(t)|\left(\frac{\partial\hat{A}(t)}{\partial t} - i[\hat{A}(t), \hat{H}(t)]\right)|\Psi(t)\rangle, \tag{2.5}$$

we obtain for the time-dependent density the well-known continuity equation

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t) = -i\langle\Psi(t)|[\hat{\rho}(\mathbf{r}), \hat{H}(t)]|\Psi(t)\rangle = -\nabla\cdot\mathbf{j}_p(\mathbf{r}, t) = -\nabla\cdot\mathbf{j}(\mathbf{r}, t), \tag{2.6}$$

where the paramagnetic current-density operator is defined by

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N}(\hat{\mathbf{p}}_i\delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i)\hat{\mathbf{p}}_i), \tag{2.7}$$

in which $\hat{\mathbf{p}}_i = -i\nabla_i$ is the momentum operator, and has expectation value

$$\mathbf{j}_p(\mathbf{r}, t) = \langle\Psi(t)|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi(t)\rangle = \mathbf{j}(\mathbf{r}, t). \tag{2.8}$$

We note that the current density $\mathbf{j}(\mathbf{r}, t)$ is equal to the paramagnetic current density $\mathbf{j}_p(\mathbf{r}, t)$ because we only consider external fields that can be described by scalar potentials. When we will consider general external fields the current density acquires

an extra term, the so-called diamagnetic current density. In that case also the Hamiltonian will have a different form and the continuity equation will still hold. The continuity equation gives an important constraint on time-dependent densities and current densities since it assures that there is locally a conservation of the number of particles. As we will see in the next section it plays an important role in the proof of the Runge-Gross theorem.

2.3 The Runge-Gross Theorem

The Runge-Gross theorem [3] states that two densities $\rho_1(\mathbf{r},t)$ and $\rho_2(\mathbf{r},t)$ evolving from a common initial state $|\Psi_0\rangle = |\Psi(t_0)\rangle$ and generated by external potentials $v_1(\mathbf{r},t)$ and $v_2(\mathbf{r},t)$ that both have a Taylor expansion around the initial time t_0 cannot be the same, provided that the external potentials differ by more than a purely time-dependent function, i.e.,

$$v_1(\mathbf{r},t) \neq v_2(\mathbf{r},t) + C(t). \tag{2.9}$$

We start the proof by using the constraint that the external potentials $v_1(\mathbf{r},t)$ and $v_2(\mathbf{r},t)$ have a Taylor expansion around t_0, i.e.,

$$v_1(\mathbf{r},t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_{1k}(\mathbf{r})(t-t_0)^k \tag{2.10}$$

$$v_2(\mathbf{r},t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_{2k}(\mathbf{r})(t-t_0)^k. \tag{2.11}$$

From this we see that Eq. (2.9) is equivalent to the statement that for the expansion coefficients there exists a smallest integer $k \geq 0$ for which

$$w_k = v_{1k}(\mathbf{r}) - v_{2k}(\mathbf{r}) = \frac{\partial^k}{\partial t^k}(v_1(\mathbf{r},t) - v_2(\mathbf{r},t))\bigg|_{t=t_0} \neq \text{const.} \tag{2.12}$$

We can now use the quantum mechanical equation of motion given in Eq. (2.5) for the current densities $\mathbf{j}_1(\mathbf{r},t)$ and $\mathbf{j}_2(\mathbf{r},t)$. We obtain

$$\frac{\partial}{\partial t}\mathbf{j}_1(\mathbf{r},t) = \frac{\partial}{\partial t}\langle\Psi_1(t)|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi_1(t)\rangle = -i\langle\Psi_1(t)|[\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}_1(t)]|\Psi_1(t)\rangle \tag{2.13}$$

$$\frac{\partial}{\partial t}\mathbf{j}_2(\mathbf{r},t) = \frac{\partial}{\partial t}\langle\Psi_2(t)|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi_2(t)\rangle = -i\langle\Psi_2(t)|[\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}_2(t)]|\Psi_2(t)\rangle \tag{2.14}$$

Since the wave functions $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ evolve from the same initial state we have that $|\Psi_1(t_0)\rangle = |\Psi_2(t_0)\rangle = |\Psi_0\rangle$ and therefore we can write

$$\begin{aligned}\frac{\partial}{\partial t}(\mathbf{j}_1(\mathbf{r},t) - \mathbf{j}_2(\mathbf{r},t))\Big|_{t=t_0} &= -i\langle\Psi_0|[\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}_1(t_0) - \hat{H}_2(t_0)]|\Psi_0\rangle \\ &= -\rho_0(\mathbf{r})\nabla(v_1(\mathbf{r},t_0) - v_2(\mathbf{r},t_0)), \end{aligned} \tag{2.15}$$

where $\rho_0(\mathbf{r}) = \rho(\mathbf{r},t_0)$ is the initial density. If condition (2.12) is satisfied for $k=0$ then the right-hand side of Eq. (2.15) cannot vanish and the current densities $\mathbf{j}_1(\mathbf{r},t)$ and $\mathbf{j}_2(\mathbf{r},t)$ will become different infinitesimally later then t_0. If condition (2.12) is not satisfied for $k=0$ then one can always find a smallest $k>0$ for which it is satisfied. Applying Eq. (2.5) $k+1$ times we obtain

$$\left(\frac{\partial}{\partial t}\right)^{k+1}(\mathbf{j}_1(\mathbf{r},t) - \mathbf{j}_2(\mathbf{r},t))\Big|_{t=t_0} = -\rho_0(\mathbf{r})\nabla w_k(\mathbf{r}) \neq 0 \tag{2.16}$$

We can therefore conclude that $\mathbf{j}_1(\mathbf{r},t) \neq \mathbf{j}_2(\mathbf{r},t)$. To prove an analogous statement for the corresponding densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ we make use of the continuity equation. We have

$$\frac{\partial}{\partial t}(\rho_1(\mathbf{r},t) - \rho_2(\mathbf{r},t)) = -\nabla\cdot(\mathbf{j}_1(\mathbf{r},t) - \mathbf{j}_2(\mathbf{r},t)). \tag{2.17}$$

Taking the derivative of the above expression $k+1$ times at $t=t_0$ we arrive at

$$\left(\frac{\partial}{\partial t}\right)^{k+2}(\rho_1(\mathbf{r},t) - \rho_2(\mathbf{r},t))\Big|_{t=t_0} = \nabla\cdot(\rho_0(\mathbf{r})\nabla w_k(\mathbf{r})). \tag{2.18}$$

To prove that the densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ will become different infinitesimally later than t_0 we have to show that the right-hand side of Eq. (2.18) cannot vanish identically. Therefore, consider the integral

$$\begin{aligned}\int d\mathbf{r}\rho_0(\mathbf{r})(\nabla w_k(\mathbf{r}))^2 = &- \int d\mathbf{r} w_k(\mathbf{r})\nabla\cdot(\rho_0(\mathbf{r})\nabla w_k(\mathbf{r})) \\ &+ \oint d\mathbf{S}\cdot(\rho_0(\mathbf{r})w_k(\mathbf{r})\nabla w_k(\mathbf{r})), \end{aligned} \tag{2.19}$$

where we used Green's theorem.

For physically realistic potentials, i.e., potentials that arise from normalizable external charge densities, the $w_k(\mathbf{r})$'s go to zero at least as $1/r$ at large distance and the density itself decays exponentially. As a consequence the surface integral vanishes for these potentials . This immediately leads to the conclusion that $\nabla\cdot(\rho_0(\mathbf{r})\nabla w_k(\mathbf{r})) \neq 0$ because if it were equal to zero, it would imply that $(\nabla w_k)^2 = 0$ which is in contradiction to the assumption made in (2.12) that $w(\mathbf{r})$ is not constant. This

completes the proof. We note that in the case of an extended system defined as a finite system with a volume approaching infinity the Runge-Gross proof holds for all volumes.

Another important result can be obtained from the Runge-Gross proof. According to Eq. (2.18) the difference $\rho_1(\mathbf{r},t) - \rho_2(\mathbf{r},t)$ is linear in $w_k(\mathbf{r})$. Hence, this difference is already nonvanishing to first order in $v_1(\mathbf{r},t) - v_2(\mathbf{r},t)$. This ensures that the linear density response function is invertible.

The constraint that the two densities should evolve from the same initial state leaves open the possibility that there are two potentials that differ by more than a constant yielding the same density but evolve from different initial states. We note that if the system is initially in its ground state the Hohenberg-Kohn theorem guarantees that the initial state is uniquely determined by the initial density [1]. Furthermore, we note that the constraint that the external potentials should have a Taylor expansion around the initial time t_0 excludes potentials that are adiabatically switched on, since they do not have a Taylor expansion around $t_0 = -\infty$.

For a given initial state Ψ_0 we have shown that the time-dependent density $\rho(\mathbf{r},t)$ uniquely determines the time-dependent external potential $v(\mathbf{r},t)$ up to a purely time-dependent function. Since the external potential determines the time-dependent wave function $|\Psi\rangle$ it can be regarded as a functional of the time-dependent density that is unique up to a purely time-dependent phase. Therefore, the expectation value of any quantum mechanical operator $\hat{A}(t)$ is a unique functional of the density according to

$$A[\rho](t) = \langle \Psi[\rho](t) | \hat{A}(t) | \Psi[\rho](t) \rangle, \tag{2.20}$$

since the ambiguity of the phase cancels out.

An important generalization of the Runge-Gross theorem was given by van Leeuwen [38]. The van Leeuwen theorem can be summarized in the following statement:

Let $\hat{H}_1$ and $\hat{H}_2$ be two Hamiltonians with different two-particle interactions $\hat{W}_1$ and $\hat{W}_2$ and different external potentials $v_1(\mathbf{r},t)$ and $v_2(\mathbf{r},t)$ that both have a Taylor expansion around the initial time t_0. Let $\rho(\mathbf{r},t)$ be the density that evolves from the initial state $|\Psi_1(t_0)\rangle$ under the influence of $\hat{H}_1$ and let $|\Psi_2(t_0)\rangle$ be an initial state of finite momentum with the same density and the same initial time-derivative of the density. Then the time-dependent density $\rho(\mathbf{r},t)$ uniquely determines, up to a purely time-dependent function, the external potential $v_2(\mathbf{r},t)$ that generates $\rho(\mathbf{r},t)$ evolving from $|\Psi_2(t_0)\rangle$ under the influence of $\hat{H}_2$.

We will not prove this theorem here. However, we will proof a generalization of this theorem by Vignale in section 2.6. It can easily be seen that in the case

$|\Psi_1(t_0)\rangle = |\Psi_2(t_0)\rangle$ and $\hat{W}_1 = \hat{W}_2$ the van Leeuwen theorem reduces to the Runge-Gross theorem. Now consider the case $\hat{W}_2 = 0$. Then the theorem asserts that for a given initial state $|\Psi_2(t_0)\rangle$ of finite momentum with the correct density and initial time-derivative of the density there is a unique potential $v_s(\mathbf{r}, t)$ (up to a purely time-dependent function) in a noninteracting system that generates the given density $\rho(\mathbf{r}, t)$ at all times. Therefore, if we can find an initial state with the correct properties mentioned above we have solved the noninteracting v-representability problem. Whether this initial state can be chosen to be the ground state of a non-interacting system is equivalent to the unresolved noninteracting v-representability problem of stationary DFT. The above result gives a good basis for the construction of the time-dependent Kohn-Sham equations.

2.4 Time-Dependent Kohn-Sham Theory

In this section our goal is to generalize the Kohn-Sham equations of stationary DFT in such a way that they generate the time-dependent densities at all times. From the previous section we know that, under some assumptions, there exists for any interacting system with time-dependent density $\rho(\mathbf{r}, t)$ a noninteracting system that yields the same time-dependent density. Furthermore, the external potential $v_s(\mathbf{r}, t)$ that generates this density in the noninteracting system is unique and therefore $v_s(\mathbf{r}, t)$ is a unique functional (up to a purely time-dependent function) of $\rho(\mathbf{r}, t)$. In analogy with stationary Kohn-Sham theory it can be written as

$$v_s(\mathbf{r}, t) = v(\mathbf{r}, t) + \int d\mathbf{r}' \rho(\mathbf{r}', t) w(|\mathbf{r} - \mathbf{r}'|) + v_{xc}(\mathbf{r}, t). \tag{2.21}$$

We now make the assumption that the initial state of the noninteracting system can be written as a single Slater determinant. Usually this will be the ground-state Kohn-Sham wave function obtained from stationary DFT. The time-dependent Kohn-Sham equations then take the form

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t) = \left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}, t)\right)\phi_i(\mathbf{r}, t), \tag{2.22}$$

$$\rho(\mathbf{r}, t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}, t)|^2. \tag{2.23}$$

So for a given approximation of $v_{xc}(\mathbf{r}, t)$ we can construct $v_s(\mathbf{r}, t)$ from the initial density which can then be used to compute the density at an infinitesimally later time, and so on.

In stationary DFT approximations for the exchange-correlation potential can be obtained from the knowledge that it is the functional derivative of the exchange-correlation energy functional with respect to the density. Unfortunately, it turns out that in time-dependent DFT it is not possible to write $v_{xc}(\mathbf{r},t)$ as the functional derivative with respect to the density of any functional. This can be understood from the following argument. Assume that $v_{xc}(\mathbf{r},t)$ can be written as the functional derivative with respect to the density of some action functional $\mathcal{A}_{xc}[\rho]$ according to

$$v_{xc}(\mathbf{r},t) = \frac{\delta \mathcal{A}_{xc}[\rho]}{\delta \rho(\mathbf{r},t)}. \tag{2.24}$$

However, this equation implies that

$$\frac{\delta v_{xc}(\mathbf{r},t)}{\delta \rho(\mathbf{r}',t')} = \frac{\delta^2 \mathcal{A}_{xc}[\rho]}{\delta \rho(\mathbf{r},t)\delta \rho(\mathbf{r}',t')}. \tag{2.25}$$

Since the right-hand side is symmetric under the interchange of the coordinates $\mathbf{r},t$ and $\mathbf{r}',t'$, the left-hand side must also be symmetric for this equation to hold. However, we know from the principle of causality that the Kohn-Sham potential $v_s(\mathbf{r},t)$ only depends on the density $\rho(\mathbf{r}',t')$ for times $t' < t$. This means that the left-hand side of Eq. (2.25) should vanish for $t' > t$ which is in contradiction to the symmetry requirement. From this we conclude that $v_{xc}(\mathbf{r},t)$ cannot be written as the functional derivative with respect to the density of any functional. Similar arguments lead to the conclusion that the potentials $v(\mathbf{r},t)$ and $v_s(\mathbf{r},t)$ cannot be written as the functional derivative of any functional. This means that for the practical application of TDDFT we cannot use the symmetry of the action in the search for good approximations of $v_{xc}(\mathbf{r},t)$. However, some exact constraints are known for $v_{xc}(\mathbf{r},t)$ from which we can obtain approximations. We will discuss these exact constraints in section 2.8. Finally, we note that the contradiction between causality and symmetry can be resolved by the construction of an action functional defined on a Keldysh contour [39] as is shown in Ref. [20]. One can then define a functional of the time-dependent density on the contour as a Legendre transform, in a similar manner as was done in Eq. (1.32) for stationary DFT. The exchange-correlation potential on the contour can then be written as the functional derivative of this Legendre transform with respect to the density on the contour. We will discuss this approach in section 2.7 within time-dependent current-density-functional theory.

2.5 The Adiabatic Local Density Approximation

The simplest approximation for the exchange-correlation potential $v_{xc}(\mathbf{r},t)$ is the so-called adiabatic local density approximation (ALDA) which is just a simple extension

of the LDA potential we encountered in stationary DFT to include time-dependent densities. It is given by

$$v_{xc}^{ALDA}(\mathbf{r},t) = \left.\frac{d\epsilon_{xc}^{h}[\rho]}{d\rho}\right|_{\rho=\rho(\mathbf{r},t)}. \tag{2.26}$$

By comparison with Eq. (1.76) we see that $v_{xc}^{ALDA}(\mathbf{r},t)$ is equal to the functional form of $v_{xc}^{LDA}(\mathbf{r})$ evaluated at the instantaneous time-dependent density $\rho(\mathbf{r},t)$. Therefore, $v_{xc}^{ALDA}(\mathbf{r},t)$ is both local in space and local in time. Thereby it neglects so-called memory effects arising from the dependence of the exchange-correlation potential at a time t on the density at times $t' < t$. Like the LDA in stationary DFT, the ALDA gives surprisingly good results even for systems that are not slowly varying in space and time. For examples see Ref. [37] and references therein. Because of the similarity between the LDA and the ALDA, the latter suffers from some of the same shortcomings as the former, e.g., the incorrect long-range behavior.

2.6 Time-Dependent Current-Density-Functional Theory

So far we have only considered systems in which the time-dependent external field can be described by a time-dependent scalar potential $v(\mathbf{r},t)$. We will now generalize this to arbitrary time-dependent external fields. General electromagnetic fields can be represented according to the following two relations

$$\mathbf{E}(\mathbf{r},t) = \nabla v(\mathbf{r},t) - \frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t} \tag{2.27}$$

$$\mathbf{B}(\mathbf{r},t) = \nabla \times \mathbf{A}(\mathbf{r},t), \tag{2.28}$$

where $\mathbf{A}(\mathbf{r},t)$ is a vector potential, and $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$ are the electric and magnetic field, respectively. These fields are invariant under a so-called gauge transformation given by

$$\begin{aligned} v(\mathbf{r},t) &\rightarrow v(\mathbf{r},t) + \frac{\partial \Lambda(\mathbf{r},t)}{\partial t} \\ \mathbf{A}(\mathbf{r},t) &\rightarrow \mathbf{A}(\mathbf{r},t) + \nabla\Lambda(\mathbf{r},t), \end{aligned} \tag{2.29}$$

where $\Lambda(\mathbf{r},t)$ is a differentiable but otherwise arbitrary function of $\mathbf{r}$ and t. In order to leave the physical results unchanged a gauge transformation according given Eq. (2.29) should be accompanied by a transformation of the wave function according to

$$\Psi(t) \rightarrow \Psi(t) e^{-i\Lambda(\mathbf{r},t)}. \tag{2.30}$$

From the gauge transformation in Eq. (2.29) we observe that we can always eliminate the scalar potential by requiring $\Lambda(\mathbf{r},t)$ to be a solution of the differential equation

$$\frac{\partial\Lambda(\mathbf{r},t)}{\partial t} = -v(\mathbf{r},t), \tag{2.31}$$

with initial condition $\Lambda(\mathbf{r},t_0)=0$. We see that such a transformation leads to a vector potential of which a part is written as the gradient of the scalar function $\Lambda(\mathbf{r},t)$. In general, that part of the vector potential that can be written as the gradient of a scalar function is called longitudinal. This is because its Fourier transform $\mathbf{A}(\mathbf{q})$ is parallel to $\mathbf{q}$ for all $\mathbf{q}$. The remaining part of the vector potential is called transverse because its Fourier transform is perpendicular to $\mathbf{q}$ for all $\mathbf{q}$.

The time-dependent Hamiltonian now takes the form

$$\hat{H}_{\mathbf{A}}(t) = \sum_{i=1}^{N}\left(\frac{1}{2}\left[\hat{\mathbf{p}}_i + \mathbf{A}(\mathbf{r}_i,t)\right]^2\right) + \hat{V}(t) + \hat{W}, \tag{2.32}$$

where the first term on the right-hand side is just the kinetic-energy operator plus extra terms involving the vector potential $\mathbf{A}(\mathbf{r},t)$. The operators $\hat{V}(t)$ and $\hat{W}$ are defined as before. With the subscript in $\hat{H}_{\mathbf{A}}(t)$ we make explicit the dependence of the Hamiltonian on the vector potential $\mathbf{A}(\mathbf{r},t)$ in order to distinguish it from the Hamiltonian $\hat{H}(t)$ in Eq. (2.1). We can express $\hat{H}_{\mathbf{A}}(t)$ in terms of $\hat{H}(t)$ according to

$$\begin{aligned}\hat{H}_{\mathbf{A}}(t) &= \hat{H}(t) + \int d\mathbf{r}\hat{\mathbf{j}}_p(\mathbf{r})\cdot\mathbf{A}(\mathbf{r},t) + \frac{1}{2}\int d\mathbf{r}\hat{\rho}(\mathbf{r})\mathbf{A}^2(\mathbf{r},t) &(2.33)\\ &= \hat{H}(t) + \int d\mathbf{r}\hat{\mathbf{j}}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r},t) - \frac{1}{2}\int d\mathbf{r}\hat{\rho}(\mathbf{r})\mathbf{A}^2(\mathbf{r},t), &(2.34)\end{aligned}$$

where the current-density operator $\hat{\mathbf{j}}(\mathbf{r},t)$ is defined by

$$\hat{\mathbf{j}}(\mathbf{r},t) = \frac{1}{2}\sum_{i=1}^{N}(\hat{\mathbf{v}}_i(t)\delta(\mathbf{r}-\mathbf{r}_i) + \delta(\mathbf{r}-\mathbf{r}_i)\hat{\mathbf{v}}_i(t)), \tag{2.35}$$

in which the velocity operator $\hat{\mathbf{v}}_i(t)$ is given by

$$\hat{\mathbf{v}}_i(t) = \hat{\mathbf{p}}_i + \mathbf{A}(\mathbf{r}_i,t). \tag{2.36}$$

The expectation value of the current-density operator is the physical (i.e., gauge invariant) current density $\mathbf{j}(\mathbf{r},t)$ according to

$$\mathbf{j}(\mathbf{r},t) = \langle\Psi(t)|\hat{\mathbf{j}}(\mathbf{r})|\Psi(t)\rangle = \mathbf{j}_p(\mathbf{r},t) + \rho(\mathbf{r},t)\mathbf{A}(\mathbf{r},t), \tag{2.37}$$

where the second term on the right-hand side is the diamagnetic current density. Note that the continuity equation (2.6) still holds, i.e.,

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = -i\langle\Psi(t)|[\hat{\rho}(\mathbf{r}),\hat{H}_{\mathbf{A}}(t)]|\Psi(t)\rangle = -\nabla\cdot\mathbf{j}(\mathbf{r},t). \tag{2.38}$$

The question now is whether there exists an equivalent of the Runge-Gross theorem for systems under the influence of general time-dependent fields, or, even better, whether there exists an equivalent of the van Leeuwen theorem for these systems. It were Ghosh and Dhara [4, 5] that provided us with a generalization of the Runge-Gross theorem for arbitrary fields. Under similar constraints used in the proof of the Runge-Gross theorem, they showed that two current densities $\mathbf{j}_1(\mathbf{r},t)$ and $\mathbf{j}_2(\mathbf{r},t)$ evolving from a common initial state $|\Psi(t_0)\rangle$ and generated by the set of potentials $\{v_1(\mathbf{r},t),\mathbf{A}_1(\mathbf{r},t)\}$ and $\{v_2(\mathbf{r},t),\mathbf{A}_2(\mathbf{r},t)\}$, where all potentials have a Taylor expansion around the initial time t_0, cannot be the same, provided that the sets of potentials differ by more than a gauge transformation of the form (2.29). The density is then uniquely determined by the current density through the continuity equation (2.38). However, the density no longer uniquely determines the current density, i.e., the map $\rho(\mathbf{r},t) \rightarrow \mathbf{j}(\mathbf{r},t)$ does not exist. Therefore, it is more convenient to reformulate the theory in terms of the current density $\mathbf{j}(\mathbf{r},t)$ giving rise to so-called time-dependent current-density-functional theory (TDCDFT). Recently, Vignale [6] generalized the van Leeuwen theorem to include general time-dependent fields. In the following we will give the proof of this theorem. Vignale's theorem can be summarized in the following statement:

Let $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ be the density and current density of a many-particle system that evolves from an initial state $|\Psi_1(t_0)\rangle$ under the influence of the Hamiltonian

$$\hat{H}_1(t) = \sum_{i=1}^{N}\left(\frac{1}{2}\left[\hat{\mathbf{p}}_i + \mathbf{A}_1(\mathbf{r}_i,t)\right]^2\right) + \hat{V}_1(t) + \hat{W}_1, \tag{2.39}$$

where $\hat{V}_1(t)$ and $\hat{W}_1$ are the external potential operator and the two-particle operator defined in a similar way as in Eqs. (2.2) and (1.4), respectively. Let the potentials $v_1(\mathbf{r},t)$ and $\mathbf{A}_1(\mathbf{r},t)$ have Taylor expansions around the initial time t_0. Then, under reasonable assumptions defined below, the same density and current density can be obtained from a many-particle system with Hamiltonian

$$\hat{H}_2(t) = \sum_{i=1}^{N}\left(\frac{1}{2}\left[\hat{\mathbf{p}}_i + \mathbf{A}_2(\mathbf{r}_i,t)\right]^2\right) + \hat{V}_2(t) + \hat{W}_2, \tag{2.40}$$

evolving from an initial state $|\Psi_2(t_0)\rangle$ that yields the same density and current density as $|\Psi_1(t_0)\rangle$, provided that $v_2(\mathbf{r},t)$ and $\mathbf{A}_2(\mathbf{r},t)$ have a Taylor expansion around the initial time t_0. The set of potentials $\{v_2(\mathbf{r},t),\mathbf{A}_2(\mathbf{r},t)\}$ is then uniquely determined by $\{v_1(\mathbf{r},t),\mathbf{A}_1(\mathbf{r},t)\}$ and the initial states $|\Psi_1(t_0)\rangle$ and $|\Psi_2(t_0)\rangle$ up to gauge transformations of the form (2.29).

In the following proof we will assume that a gauge transformation has been done for both systems 1 and 2 with $\Lambda(\mathbf{r},t)$ a solution of Eq. (2.31), so that the scalar potentials $v_1(\mathbf{r},t)$ and $v_2(\mathbf{r},t)$ are zero for all times t. We start the proof by considering the quantum mechanical equation of motion of $\mathbf{j}(\mathbf{r},t)$ for system 1. Using Eq. (2.5) we then obtain what might be called the continuity equation for the current density,

$$\frac{\partial \mathbf{j}(\mathbf{r},t)}{\partial t} = \left\langle \frac{\partial \hat{\mathbf{j}}(\mathbf{r},t)}{\partial t} - i[\hat{\mathbf{j}}(\mathbf{r},t), \hat{H}_1(t)] \right\rangle_1 \tag{2.41}$$

$$= \rho(\mathbf{r},t)\frac{\partial \mathbf{A}_1(\mathbf{r},t)}{\partial t} - \mathbf{j}(\mathbf{r},t)\times[\nabla\times\mathbf{A}_1(\mathbf{r},t)] + \mathcal{F}_1(\mathbf{r},t) + \nabla\cdot\sigma_1(\mathbf{r},t), \tag{2.42}$$

where $\langle\hat{A}(t)\rangle_1$ denotes the expectation value of an operator $\hat{A}(t)$ at time t for system 1. The internal force density $\mathcal{F}_1(\mathbf{r},t)$ and the stress tensor $\sigma_1(\mathbf{r},t)$ are defined as

$$\mathcal{F}_1(\mathbf{r},t) = -\left\langle \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\sum_{j\neq i}^{N}\nabla_i w_1(|\mathbf{r}_i-\mathbf{r}_j|)\right\rangle_1 \tag{2.43}$$

$$\sigma_1(\mathbf{r},t) = -\left\langle \frac{1}{4}\sum_{i=1}^{N}\{\hat{v}_{1\alpha}(t),\{\hat{v}_{1\beta}(t),\delta(\mathbf{r}-\mathbf{r}_i)\}\}\right\rangle_1, \tag{2.44}$$

where $\{\hat{A},\hat{B}\} = \hat{A}\hat{B}+\hat{B}\hat{A}$ denotes the anticommutator of two operators $\hat{A}$ and $\hat{B}$. With the notation $\nabla\cdot\sigma_1(\mathbf{r},t)$ we mean that $[\nabla\cdot\sigma_1(\mathbf{r},t)]_\alpha = \sum_\beta \partial\sigma_1(\mathbf{r},t)/\partial r_\beta$. Note that in Eq. (2.42) the quantities $-\partial\mathbf{A}_1(\mathbf{r},t)/\partial t$ and $\nabla\times\mathbf{A}_1(\mathbf{r},t)$ are the electric and magnetic field, respectively, since $v_1(\mathbf{r},t)=0$ for all t. According to Vignale's theorem the same current density should also obey the following equation of motion

$$\frac{\partial \mathbf{j}(\mathbf{r},t)}{\partial t} = \rho(\mathbf{r},t)\frac{\partial \mathbf{A}_2(\mathbf{r},t)}{\partial t} - \mathbf{j}(\mathbf{r},t)\times[\nabla\times\mathbf{A}_2(\mathbf{r},t)] + \mathcal{F}_2(\mathbf{r},t) + \nabla\cdot\sigma_2(\mathbf{r},t), \tag{2.45}$$

where $\mathcal{F}_2(\mathbf{r},t)$ and $\sigma_2(\mathbf{r},t)$ are defined in an analogous manner to $\mathcal{F}_1(\mathbf{r},t)$ and $\sigma_1(\mathbf{r},t)$. The difference of the two equations of motion for the current density $\mathbf{j}(\mathbf{r},t)$ is given by

$$\rho(\mathbf{r},t)\frac{\partial \Delta\mathbf{A}(\mathbf{r},t)}{\partial t} = \mathbf{j}(\mathbf{r},t)\times[\nabla\times\Delta\mathbf{A}(\mathbf{r},t)] + Q_1(\mathbf{r},t) - Q_2(\mathbf{r},t), \tag{2.46}$$

where $\Delta\mathbf{A}(\mathbf{r},t) \equiv \mathbf{A}_2(\mathbf{r},t) - \mathbf{A}_1(\mathbf{r},t)$ and

$$Q_1(\mathbf{r},t) \equiv \mathcal{F}_1(\mathbf{r},t) + \nabla\cdot\sigma_1(\mathbf{r},t). \tag{2.47}$$

The expression for $Q_2(\mathbf{r},t)$ is analogous to that for $Q_1(\mathbf{r},t)$. Equation (2.46) determines the vector potential $\mathbf{A}_2(\mathbf{r},t)$ that yields the same current density as $\mathbf{A}_1(\mathbf{r},t)$. The question is whether Eq. (2.46) has a solution and, if so, whether this solution is

unique. For general vector potentials this is not easy to prove since Eq. (2.46) not only depends on $\mathbf{A}_2(\mathbf{r},t)$ explicitly but also implicitly through $Q_2(\mathbf{r},t)$. For this reason we required that the vector potentials $\mathbf{A}_1(\mathbf{r},t)$ and $\mathbf{A}_2(\mathbf{r},t)$ have a Taylor expansion around $t=t_0$. Also the difference of the two vector potentials, $\Delta\mathbf{A}(\mathbf{r},t)$, has a Taylor expansion around the initial time t_0 according to

$$\Delta\mathbf{A}(\mathbf{r},t)=\sum_{k=0}^{\infty}\Delta\mathbf{A}_k(\mathbf{r})(t-t_0)^k, \tag{2.48}$$

with

$$\Delta\mathbf{A}_k(\mathbf{r})\equiv\frac{1}{k!}\left.\frac{\partial^k\Delta\mathbf{A}(\mathbf{r},t)}{\partial t^k}\right|_{t=t_0}. \tag{2.49}$$

Substituting this expansion into Eq. (2.46) and equating the lth term of the expansion we obtain

$$\sum_{k=0}^{l}\rho_{l-k}(\mathbf{r})\left[\frac{\partial\Delta\mathbf{A}(\mathbf{r},t)}{\partial t}\right]_k=\sum_{k=0}^{l}\{\mathbf{j}_{l-k}(\mathbf{r},t)\times[\nabla\times\Delta\mathbf{A}_k(\mathbf{r})]\}+[Q_1(\mathbf{r},t)]_l-[Q_2(\mathbf{r},t)]_l, \tag{2.50}$$

where $\rho_k(\mathbf{r})$ and $\mathbf{j}_k(\mathbf{r})$ are the kth coefficients in the Taylor expansions of $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ around $t=t_0$ and $[f(\mathbf{r},t)]_l$ is the lth coefficient (a function of $\mathbf{r}$ alone) in the Taylor expansion of a function $f(\mathbf{r},t)$ around $t=t_0$. It is a consequence of the analyticity of the vector potential and the time-dependent Schrödinger equation (2.1) that all the quantities entering Eq. (2.50) have a Taylor expansion around $t=t_0$. Since we have that

$$\left[\frac{\partial\Delta\mathbf{A}(\mathbf{r},t)}{\partial t}\right]_k=(k+1)\Delta\mathbf{A}_{k+1}(\mathbf{r}), \tag{2.51}$$

we can write Eq. (2.50) as follows

$$\begin{aligned}\rho_0(\mathbf{r})(l+1)\Delta\mathbf{A}_{l+1}(\mathbf{r})= &-\sum_{k=0}^{l-1}\rho_{l-k}(\mathbf{r})(k+1)\Delta\mathbf{A}_{k+1}(\mathbf{r})\\ &+\sum_{k=0}^{l}\{\mathbf{j}_{l-k}(\mathbf{r},t)\times[\nabla\times\Delta\mathbf{A}_k(\mathbf{r})]\}\\ &+[Q_1(\mathbf{r},t)]_l-[Q_2(\mathbf{r},t)]_l,\end{aligned} \tag{2.52}$$

where the $k=l$ term of the sum in the left-hand side of Eq. (2.50) has been isolated on the left-hand side. Equation (2.52) is a recursion relation for the coefficients of the Taylor expansion of $\Delta\mathbf{A}(\mathbf{r},t)$, i.e., the coefficient $\Delta\mathbf{A}_{l+1}(\mathbf{r})$ is solely determined by the coefficients $\Delta\mathbf{A}_k(\mathbf{r})$ with $k\leq l$. This is clear for the coefficients that enter Eq. (2.52) explicitly. For the coefficients $\Delta\mathbf{A}_k(\mathbf{r})$ that enter Eq. (2.52) implicitly

through the coefficients of the expansion of $Q_2(\mathbf{r},t)$ this is a consequence of the time-dependend Schrödinger equation (2.1). Since it is of first order in time it guarantees that the lth coefficient in the expansion of the states $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ are solely determined by the coefficients $\Delta\mathbf{A}_k(\mathbf{r})$ with $k<l$. This means that if we know the initial value of $\Delta\mathbf{A}_k(\mathbf{r})$, i.e., $\Delta\mathbf{A}(\mathbf{r},t)=\Delta\mathbf{A}_2(\mathbf{r},0)-\Delta\mathbf{A}_1(\mathbf{r},0)$, we can determine all coefficients through the recursion relation (2.52). This initial value can easily be determined from the knowledge that the density and current density of systems 1 and 2 are equal. Therefore, we see from Eq. (2.37) that

$$\rho(\mathbf{r},t_0)\Delta\mathbf{A}_0(\mathbf{r})=\langle\Psi_2(t_0)|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi_2(t_0)\rangle-\langle\Psi_1(t_0)|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi_1(t_0)\rangle, \tag{2.53}$$

where the paramagnetic current-density operator is defined in Eq. (2.7). The recursion relation (2.52) in combination with initial condition (2.53) now completely determines the coefficients in the Taylor expansion of vector potential $\mathbf{A}_2(\mathbf{r},t)$ that yields, in system 2, the same density $\rho(\mathbf{r},t)$ and current density $\mathbf{j}(\mathbf{r},t)$ as the vector potential $\mathbf{A}_1(\mathbf{r},t)$ yields in system 1. Since we required that $\mathbf{A}_1(\mathbf{r},t)$ and $\mathbf{A}_2(\mathbf{r},t)$ have a Taylor expansion around $t=t_0$, the coefficients in the Taylor expansion completely determine $\mathbf{A}_2(\mathbf{r},t)$ provided that this series converges within a nonvanishing convergence radius $t_c>0$. If this is the case then $\mathbf{A}_2(\mathbf{r},t)$ is uniquely determined, because $\mathbf{A}_2(\mathbf{r},t)$ can be determined up to t_c and then the procedure can be iterated with t_c as the initial time, and so on. If the convergence radius is zero this means that the kth derivative of $\mathbf{A}_2(\mathbf{r},t)$ with respect to time at $t=0$ grows more rapidly than $k!a^k$ with a an arbitrary positive constant. Because of the smooth dynamics of the Schrödinger equation it is very unlikely that the values of the initial derivatives will show such an explosion, and, therefore, we will exclude this option. This defines the reasonable assumptions mentioned in Vignale's theorem. We have thus proven Vignale's theorem. Note that the proof given above does not require the density or the current density to vanish at infinity.

We will now discuss two special cases of Vignale's theorem. First, let system 1 and 2 be the same, i.e., $\hat{W}_1=\hat{W}_2$ and $|\Psi_1(t_0)\rangle=|\Psi_2(t_0)\rangle$. Then, according to Eq. (2.53), $\Delta\mathbf{A}_0(\mathbf{r})=0$ and therefore, according to Eq. (2.52), $\Delta\mathbf{A}_k(\mathbf{r})=0$ for all k. This means that $\mathbf{A}_1(\mathbf{r},t)=\mathbf{A}_2(\mathbf{r},t)$ at all times t. We conclude that two vector potentials that evolve from the same initial state of a many-particle system and that yield the same current density must be equal, up to a gauge transformation. This is simply an analogue of the Runge-Gross theorem in the case of TDCDFT. Second, let system 2 be a system of noninteracting particles, i.e., $\hat{W}=0$. Then, Vignale's theorem asserts that for a given current density generated by a vector potential $\mathbf{A}_1(\mathbf{r},t)$ in an interacting system evolving from an initial state $|\Psi_1(t_0)\rangle$ there is a unique vector potential $\mathbf{A}_2(\mathbf{r},t)$ (up to a gauge transform) in a noninteracting system evolving from

an initial state $|\Psi_2(t_0)\rangle$ that yields this given current density at all times. Therefore, if we can find an initial state $|\Psi_2(t_0)\rangle$ with the correct initial density and current density we have solved the noninteracting **A**-representability problem. As mentioned before, whether this initial state can be chosen to be the ground state of a non-interacting system is equivalent to the unresolved noninteracting v-representability problem of stationary DFT. The above result gives a good basis for setting up the time-dependent Kohn-Sham equations for general time-dependent external fields. They are given by

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \left(\frac{1}{2}[\hat{\mathbf{p}}+\mathbf{A}_s(\mathbf{r},t)]^2+v_s(\mathbf{r},t)\right)\phi_i(\mathbf{r},t) \tag{2.54}$$

$$\mathbf{j}(\mathbf{r},t) = \frac{1}{2i}\sum_{i=1}^{N}[\phi_i^*(\mathbf{r},t)\nabla\phi_i(\mathbf{r},t)-\nabla\phi_i^*(\mathbf{r},t)\phi_i(\mathbf{r},t)]+\rho(\mathbf{r},t)\mathbf{A}_s(\mathbf{r},t) \tag{2.55}$$

$$\rho(\mathbf{r},t) = \sum_{i=1}^{N}|\phi_i(\mathbf{r},t)|^2, \tag{2.56}$$

where we again made the assumption that the initial state of the noninteracting system can be written as a single Slater determinant. The set of Kohn-Sham potentials $\{v_s(\mathbf{r},t),\mathbf{A}_s(\mathbf{r},t)\}$ are defined, up to a gauge transform, by

$$v_s(\mathbf{r},t) = v(\mathbf{r},t)+\int d\mathbf{r}'\rho(\mathbf{r}',t)w(|\mathbf{r}-\mathbf{r}'|)+v_{xc}(\mathbf{r},t) \tag{2.57}$$

$$\mathbf{A}_s(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t)+\mathbf{A}_{xc}(\mathbf{r},t). \tag{2.58}$$

We note that it has been shown that an interacting system under the influence of a time-dependent field that can be described by a scalar potential only, cannot, in general, be described by a Kohn-Sham system with solely a scalar potential [40]. That is, a v-representable current density is, in general, not noninteracting v-representable. However, the v-representable current density might be noninteracting **A**-representable since this is a much weaker condition. In the next section we will show that the potentials in Eqs. (2.57) and (2.58) can be written as functional derivatives with respect to the current density of the Legendre transform of an action functional defined on the Keldysh contour as was shown in Ref. [41].

2.7 The Keldysh Action Functional

Let us start this section by introducing the time-evolution operator $\hat{U}(t,t')$. It relates a state at time t' to a state at time t according to

$$|\Psi(t)\rangle = \hat{U}(t,t')|\Psi(t')\rangle. \tag{2.59}$$

From this expression we can derive that

$$\hat{U}(t,t') = \hat{T}\exp\left[-i\int_{t'}^{t} d\tau \hat{H}(\tau)\right], \tag{2.60}$$

where $\hat{T}$ is the time-ordering operator given by

$$\begin{aligned}\hat{T}\left[\hat{H}(\tau_1)\cdots\hat{H}(\tau_n)\right] &= \sum_P \Theta(\tau_{P(1)}-\tau_{P(2)})\cdots\Theta(\tau_{P(n-1)}-\tau_{P(n)}) \\ &\times \hat{H}(\tau_{P(1)})\cdots\hat{H}(\tau_{P(n)}),\end{aligned} \tag{2.61}$$

where P runs over all permutations of the numbers $1\cdots n$. If the Hamiltonian is time independent the evolution operator is simply given by

$$\hat{U}(t,t') = \exp\left[-i\hat{H}(t-t')\right]. \tag{2.62}$$

The time-evolution operator has the following properties

$$\hat{U}(t,t) = 1 \tag{2.63}$$

$$i\frac{\partial}{\partial t}\hat{U}(t,t') = \hat{H}(t)\hat{U}(t,t') \tag{2.64}$$

$$-i\frac{\partial}{\partial t}\hat{U}(t',t) = \hat{U}(t',t)\hat{H}(t). \tag{2.65}$$

The first property is obvious from Eq. (2.59). The second property is obtained by taking the derivative of Eq. (2.59) with respect to t and using the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle. \tag{2.66}$$

This gives the result

$$i\frac{\partial}{\partial t}\hat{U}(t,t')|\Psi(t')\rangle = \hat{H}(t)\hat{U}(t,t')|\Psi(t')\rangle. \tag{2.67}$$

Since $|\Psi(t')\rangle$ is arbitrary we obtain Eq. (2.64). In a similar way we can obtain Eq. (2.65) by taking the time-derivative of Eq. (2.59) with respect to t'.

Consider a system that is described by the time-dependent Hamiltonian $\hat{H}_0(t)$ that has initial state $|\Psi_0\rangle$. At a certain time $t = t_0$ we switch on the time-dependent perturbation $\delta\hat{H}(t)$. The full time-dependent Hamiltonian $\hat{H}(t)$ then reads

$$\hat{H}(t) = \hat{H}_0(t) + \delta\hat{H}(t), \tag{2.68}$$

where $\delta H(t) = 0$ for $t < t_0$. The time-evolution operator can now be written as

$$\hat{U}'(t,t_0) = \hat{U}(t,t_0) + \delta\hat{U}(t,t_0). \tag{2.69}$$

Using Eqs. (2.63), (2.64), and (2.65) we obtain to first order in the perturbation

$$
\begin{aligned}
i\frac{\partial}{\partial t}\delta\hat{U}(t,t_0) &= \hat{H}_0(t)\delta\hat{U}(t,t_0) + \delta\hat{H}(t)\hat{U}(t,t_0) && (2.70)\\
-i\frac{\partial}{\partial t}\delta\hat{U}(t_0,t) &= \delta\hat{U}(t_0,t)\hat{H}_0(t) + \hat{U}(t_0,t)\delta\hat{H}(t) && (2.71)\\
\delta\hat{U}(t,t) &= 0. && (2.72)
\end{aligned}
$$

The above set of equations has the following solution

$$
\delta\hat{U}(t,t_0) = -i\int_{t_0}^{t} dt'\hat{U}(t,t')\delta\hat{H}(t')\hat{U}(t',t_0). \tag{2.73}
$$

We now define an operator $\hat{A}(t)$ in the Heisenberg picture as

$$
\hat{A}_H(t) = \hat{U}(t_0,t)\hat{A}(t)\hat{U}(t,t_0). \tag{2.74}
$$

The expectation value of the operator $\hat{A}(t)$ at time t can now be written as

$$
\langle\hat{A}(t)\rangle = \langle\Psi_0|\hat{A}_H(t)|\Psi_0\rangle = \langle\Psi_0|\hat{U}(t_0,t)\hat{A}(t)\hat{U}(t,t_0)|\Psi_0\rangle \tag{2.75}
$$

If we read the expression on the right-hand side from right to left we can say that the system evolves from t_0 to t after which the operator $\hat{A}(t)$ acts on the system and then the system evolves back again from t to t_0. A corresponding contour was introduced by Keldysh [39]. Using this contour we can write the following generalization for the expectation value of $\hat{A}(t)$

$$
\langle\hat{A}(t)\rangle = \frac{\langle\Psi_0|\hat{T}_C\left[\exp\left(-i\int_C d\tau\hat{H}(\tau)\right)\hat{A}(t)\right]|\Psi_0\rangle}{\langle\Psi_0|\hat{T}_C\left[\exp\left(-i\int_C d\tau\hat{H}(\tau)\right)\right]|\Psi_0\rangle} \tag{2.76}
$$

where we defined

$$
\begin{aligned}
\hat{T}_C\left[\exp\left(-i\int_C d\tau\hat{H}(\tau)\right)\hat{A}(t)\right] &\equiv \sum_n^{\infty}\frac{(-i)^n}{n!}\int_C d\tau_1\cdots d\tau_n \\
&\times\ \hat{T}_C\left[\hat{A}(t)\hat{H}(\tau_1)\cdots\hat{H}(\tau_n)\right]. \qquad (2.77)
\end{aligned}
$$

Here $\hat{T}_C$ is the time-ordering operator on the contour defined by

$$
\begin{aligned}
\hat{T}_C\left[\hat{A}_1(\tau_1)\cdots\hat{A}_n(\tau_n)\right] &= \sum_P \Theta_C(\tau_{P(1)},\tau_{P(2)})\cdots\Theta_C(\tau_{P(n-1)},\tau_{P(n)}) \\
&\times\ \hat{A}_{P(1)}(\tau_{P(1)})\cdots\hat{A}_{P(n)}(\tau_{P(n)}), \qquad (2.78)
\end{aligned}
$$

where $\Theta_C(t,t')$ is a generalization of the Heavside step function for time arguments that are on the contour, i.e., it is equal to 1 if time t is later than time t' on the contour and zero otherwise. In Eq. (2.76) we extended the definition of the Hamiltonian in such a way that it can be different on the forward and backward parts of the contour. If the Hamiltonian $H(t)$ is the same on the forward and backward parts of the contour, which is the case for physical perturbations, Eq. (2.76) reduces to Eq. (2.75).

Let us now consider systems under the influence of general time-dependent fields, i.e., systems that are described by the Hamiltonian in Eq. (2.32). We choose the gauge such that all perturbations are included in the vector potential, that is, for the scalar potential we have $v(\mathbf{r},t) = v(\mathbf{r},t_0)$ for all times t. We can therefore rewrite $H(t)$ according to

$$H(t) = \hat{H}_0(t) + \sum_{i=1}^{N} \frac{1}{2}\hat{\mathbf{p}}_i \cdot \mathbf{A}(\mathbf{r}_i,t) + \frac{1}{2}\mathbf{A}(\mathbf{r}_i,t)\cdot\hat{\mathbf{p}}_i + \frac{1}{2}\mathbf{A}^2(\mathbf{r}_i,t) \tag{2.79}$$

$$= \hat{H}_0(t) + \int d\mathbf{r}\hat{\mathbf{j}}_p(\mathbf{r})\cdot\mathbf{A}(\mathbf{r},t) + \frac{1}{2}\int d\mathbf{r}\hat{\rho}(\mathbf{r})\mathbf{A}^2(\mathbf{r},t). \tag{2.80}$$

We now define the following action functional of the vector potential $\mathbf{A}(\mathbf{r},t)$

$$\tilde{\mathcal{A}}[\mathbf{A}] = i\ln\langle\Psi_0|\hat{U}(t_0,t_0)|\Psi_0\rangle, \tag{2.81}$$

where we generalized the expression for the evolution operator to times on the contour according to

$$\hat{U}(t,t') = \hat{T}_C \exp\left(-i\int_{t'}^{t} d\tau \hat{H}(\tau)\right). \tag{2.82}$$

Since the Hamiltonian is a functional of the vector potential $\mathbf{A}(\mathbf{r},t)$ it is clear that if $\mathbf{A}(\mathbf{r},t)$ is the same on the forward and backward parts of the contour then $\hat{U}(t_0,t_0) = 1$ and the action functional vanishes. We will denote vector potentials of this kind as physical vector potentials. However, the functional derivatives of $\tilde{\mathcal{A}}[\mathbf{A}]$ with respect to $\mathbf{A}(\mathbf{r},t)$ taken at a physical vector potentials is, in general, nonzero. With the definition of the evolution operator in Eq. (2.83) we can rewrite Eq. (2.76) for the expectation value of $\hat{A}(t)$ as

$$\langle\hat{A}(t)\rangle = \frac{\langle\Psi_0|\hat{A}_H(t)|\Psi_0\rangle}{\langle\Psi_0|\hat{U}(t_0,t_0)|\Psi_0\rangle}. \tag{2.83}$$

From Eqs. (2.73) and (2.80) it is easy to see that the functional derivative of $\hat{U}(t,t_0)$ with respect to $\mathbf{A}(\mathbf{r},t)$ is given by

$$\frac{\delta\hat{U}(t,t_0)}{\delta\mathbf{A}(\mathbf{r},t')} = -i\hat{U}(t,t')\left[\hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\rho}(\mathbf{r})\mathbf{A}(\mathbf{r},t')\right]\hat{U}(t',t_0) \tag{2.84}$$

With this result we obtain for the functional derivative of $\tilde{\mathcal{A}}[\mathbf{A}]$ with respect to $\mathbf{A}(\mathbf{r},t)$

$$\frac{\delta\tilde{\mathcal{A}}[\mathbf{A}]}{\delta\mathbf{A}(\mathbf{r},t)} = \frac{\langle\Psi_0|\hat{U}(t_0,t)\left[\hat{\mathbf{j}}_p(\mathbf{r})+\hat{\rho}(\mathbf{r})\mathbf{A}(\mathbf{r},t)\right]\hat{U}(t,t_0)|\Psi_0\rangle}{\langle\Psi_0|\hat{U}(t_0,t_0)|\Psi_0\rangle} \tag{2.85}$$

$$= \langle\hat{\mathbf{j}}_p(\mathbf{r},t)\rangle + \langle\hat{\rho}(\mathbf{r},t)\rangle\mathbf{A}(\mathbf{r},t) = \mathbf{j}(\mathbf{r},t). \tag{2.86}$$

From the above equation we see that the vector potential and the current density are conjugate variables. In a similar way as in stationary DFT we can now define the Legendre transform

$$\mathcal{A}[\mathbf{j}] = -\tilde{\mathcal{A}}[\mathbf{A}] + \int_C dtd\mathbf{r}\mathbf{j}(\mathbf{r},t)\cdot\mathbf{A}(\mathbf{r},t), \tag{2.87}$$

so that

$$\frac{\delta\mathcal{A}[\mathbf{j}]}{\delta\mathbf{j}(\mathbf{r},t)} = \mathbf{A}(\mathbf{r},t). \tag{2.88}$$

The Legendre transformation assumes that the current density uniquely determines the vector potential and vice versa which means that Eq. (2.86) should be invertible (up to a gauge). It can be proved by a generalization of the proof given in Ref. [20] for the density-density response function that for switch-on processes the Keldysh current-current response function is invertible for systems initially in their ground state. Similarly we have for the noninteracting Kohn-Sham system the Legendre transform

$$\mathcal{A}_s[\mathbf{j}] = -\tilde{\mathcal{A}}_s[\mathbf{A}] + \int_C dtd\mathbf{r}\mathbf{j}(\mathbf{r},t)\cdot\mathbf{A}_s(\mathbf{r},t) \tag{2.89}$$

We can now define the exchange-correlation part of the action functional $\mathcal{A}_{xc}$ by

$$\mathcal{A}[\mathbf{j}] = \mathcal{A}_s[\mathbf{j}] - \mathcal{A}_{xc}[\mathbf{j}] - \frac{1}{2}\int_C dtd\mathbf{r}d\mathbf{r}'\rho(\mathbf{r},t)\rho(\mathbf{r}',t)w(|\mathbf{r}-\mathbf{r}'|), \tag{2.90}$$

where the density $\rho(\mathbf{r},t)$ is a functional of the initial state and of the current density through the generalization of the continuity equation for times on the contour. In Eq. (2.90) we assume that $\mathcal{A}[\mathbf{j}]$ and $\mathcal{A}_s[\mathbf{j}]$ are defined on the same domain of current densities, i.e., $\mathbf{j}(\mathbf{r},t)$ is noninteracting $\mathbf{A}$-representable. In other words, we assume that there exists a generalization of Vignale's theorem for times on the contour. Taking the functional derivative of Eq. (2.90) with respect to the current density $\mathbf{j}(\mathbf{r},t)$ leads to

$$\mathbf{A}_s(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t) + \mathbf{A}_{xc}(\mathbf{r},t) + \mathbf{A}_W(\mathbf{r},t), \tag{2.91}$$

where $\mathbf{A}_W(\mathbf{r},t)$ is defined by

$$\frac{\partial\mathbf{A}_W(\mathbf{r},t)}{\partial t} = -\nabla\int d\mathbf{r}\rho(\mathbf{r}',t)w(|\mathbf{r}-\mathbf{r}'|), \tag{2.92}$$

and the exchange-correlation vector potential is given by

$$\mathbf{A}_{xc}(\mathbf{r},t) = \frac{\delta \mathcal{A}_{xc}}{\delta \mathbf{j}(\mathbf{r},t)}. \tag{2.93}$$

It is easy to see that Eq. (2.91) and Eqs. (2.57) and (2.58) are the same up to a gauge transformation.

Finally, let us take a look at the causality and symmetry properties of the current-current response function on the contour. These properties have led to the paradox discussed in section 2.4 which led to the conclusion that it is not possible to write the scalar potentials $v(\mathbf{r},t)$, $v_s(\mathbf{r},t)$ and $v_{xc}(\mathbf{r},t)$ as functional derivatives with respect to the density of any functional. We will now show that this paradox is resolved in the case of the Keldysh action functional. In the following we will show the proof of this for the vector potential $\mathbf{A}(\mathbf{r},t)$. The proof for other potentials is analogous. From Eq. (2.85) we obtain for the current-current response function on the contour

$$\begin{aligned}
\chi_{C,mn}(\mathbf{r},t,\mathbf{r}',t') &= \frac{\delta^2 \tilde{\mathcal{A}}[\mathbf{A}]}{\delta A_m(\mathbf{r},t)\delta A_n(\mathbf{r}',t')} \\
&= \delta_{mn}\rho(\mathbf{r},t)\delta_C(t,t')\delta(\mathbf{r}-\mathbf{r}') \\
&- i\Theta_C(t,t')\langle \hat{\mathbf{j}}_p(\mathbf{r},t)\hat{\mathbf{j}}_p(\mathbf{r}',t')\rangle - i\Theta_C(t',t)\langle \hat{\mathbf{j}}_p(\mathbf{r}',t')\hat{\mathbf{j}}_p(\mathbf{r},t)\rangle \\
&+ i\langle \hat{\mathbf{j}}_p(\mathbf{r},t)\rangle\langle \hat{\mathbf{j}}_p(\mathbf{r}',t')\rangle,
\end{aligned} \tag{2.94}$$

where $\delta_C(t,t') = \partial_t \Theta_C(t,t')$ is the generalization of the delta function to times on the contour and we defined

$$\langle \hat{A}(t)\hat{B}(t')\rangle = \frac{\langle \Psi_0|\hat{A}_H(t)\hat{B}_H(t')|\Psi_0\rangle}{\langle \Psi_0|\hat{U}(t_0,t_0)|\Psi_0\rangle}. \tag{2.95}$$

The last term in Eq. (2.94) is due to the functional differentiation of the denominator in Eq. (2.85). If we define the fluctuation operator

$$\Delta\hat{\mathbf{j}}_p(\mathbf{r},t) = \hat{\mathbf{j}}_p(\mathbf{r},t) - \langle \hat{\mathbf{j}}_p(\mathbf{r},t)\rangle \tag{2.96}$$

we can rewrite Eq. (2.94) as

$$\chi_{C,mn}(\mathbf{r},t,\mathbf{r}',t') = \delta_{mn}\rho(\mathbf{r},t)\delta_C(t,t')\delta(\mathbf{r}-\mathbf{r}') - i\langle T_C[\Delta\hat{\mathbf{j}}_p(\mathbf{r},t)\Delta\hat{\mathbf{j}}_p(\mathbf{r}',t')]\rangle. \tag{2.97}$$

We observe that the current-current response function is a symmetric function of its arguments which it should be since it is a second order functional derivative. We will now show that it becomes a retarded function for physical current densities, i.e., current densities that are generated by physical vector potentials. The current density

response can be obtained from the current-current response function according to

$$\begin{aligned}\delta j_m(\mathbf{r},t) &= \sum_n \int_C dt' d\mathbf{r}' \chi_{C,mn}(\mathbf{r},t,\mathbf{r}',t')\delta A_n(\mathbf{r}',t') \\ &= \rho_0(\mathbf{r})\delta A_m(\mathbf{r},t) \\ &- \sum_n i\int_{t_0}^{t} dt' d\mathbf{r}' \langle \Delta\hat{\mathbf{j}}_{p,m}(\mathbf{r},t)\Delta\hat{\mathbf{j}}_{p,n}(\mathbf{r}',t')\rangle \delta A_n(\mathbf{r}',t') \\ &- \sum_n i\int_{t}^{t_0} dt' d\mathbf{r}' \langle \Delta\hat{\mathbf{j}}_{p,n}(\mathbf{r}',t')\Delta\hat{\mathbf{j}}_{p,m}(\mathbf{r},t)\rangle \delta A_n(\mathbf{r}',t') \qquad (2.98)\end{aligned}$$

For physical current densities this can be written according to

$$\delta j_m(\mathbf{r},t) = \sum_n \int_{t_0}^{\infty} dt' d\mathbf{r}' \chi_{mn}(\mathbf{r},t,\mathbf{r}',t')\delta A_n(\mathbf{r}',t'), \qquad (2.99)$$

where

$$\begin{aligned}\chi_{mn}(\mathbf{r},t,\mathbf{r}',t') &= \delta_{mn}\rho_0(\mathbf{r})\delta(t-t')\delta(\mathbf{r}-\mathbf{r}') \\ &- i\Theta(t-t')\langle\Psi_0|[\hat{\mathbf{j}}_{p,m}(\mathbf{r},t)_{H_0},\hat{\mathbf{j}}_{p,n}(\mathbf{r}',t')_{H_0}]|\Psi_0\rangle. \qquad (2.100)\end{aligned}$$

Here we used that the expectation value of the commutator of the fluctuation operators for the paramagnetic current density is the same as the expectation value of the commutator of the paramagnetic current operators. The function $\chi_{mn}(\mathbf{r},t,\mathbf{r}',t')$ is the retarded current-current response function as it usually appears in response theory. In the next section we will discuss some exact constraints that are known for the set of exchange-correlation potentials $\{v_{xc}(\mathbf{r},t),\mathbf{A}_{xc}(\mathbf{r},t)\}$.

2.8 Exact Constraints

In accordance with Newton's third law the net force and net torque acting on a system should have no contribution from the system itself. Since the net force and the net torque due to the potential corresponding to the two-particle interaction are equal to zero, the net force and the net torque due to the set of exchange correlation potentials $\{v_{xc}(\mathbf{r},t),\mathbf{A}_{xc}(\mathbf{r},t)\}$ should be equal to zero as well [42]. This leads to constraints on the form of $\{v_{xc}(\mathbf{r},t),\mathbf{A}_{xc}(\mathbf{r},t)\}$. These constraints are made explicit by the zero-force and zero-torque theorems which read

$$\mathbf{F}_{xc}(t) = \int d\mathbf{r}[\rho(\mathbf{r},t)\mathbf{E}_{xc}(\mathbf{r},t) + \mathbf{j}(\mathbf{r},t)\times\mathbf{B}_{xc}(\mathbf{r},t)] = 0 \qquad (2.101)$$

$$\mathbf{T}_{xc}(t) = \int d\mathbf{r}[\rho(\mathbf{r},t)\mathbf{r}\times\mathbf{E}_{xc}(\mathbf{r},t) + \mathbf{r}\times(\mathbf{j}(\mathbf{r},t)\times\mathbf{B}_{xc}(\mathbf{r},t))] = 0, \qquad (2.102)$$

where $\mathbf{F}_{xc}(t)$ and $\mathbf{T}_{xc}(t)$ are the exchange-correlation parts of the force and the torque, respectively. The exchange-correlation parts of the electric and magnetic fields are analogous to Eqs. (2.27) and (2.28). They are given by

$$\mathbf{E}_{xc}(\mathbf{r},t) = \nabla v_{xc}(\mathbf{r},t) - \frac{\partial}{\partial t}\mathbf{A}_{xc}(\mathbf{r},t) \tag{2.103}$$

$$\mathbf{B}_{xc}(\mathbf{r},t) = \nabla \times \mathbf{A}_{xc}(\mathbf{r},t). \tag{2.104}$$

We note that if the zero-force theorem is satisfied this automatically guarantees that the harmonic-potential theorem is satisfied. The harmonic-potential theorem states that the density of a system of electrons confined in a static parabolic potential well follows rigidly the classical motion of the center of mass when subjected to a uniform time-dependent perturbation [43].

Another constraint on the form of the exchange-correlation potentials is the so-called generalized translational invariance which, up to a gauge transform, can be expressed as

$$v_{xc}[\mathbf{j}'](\mathbf{r},t) = v_{xc}[\mathbf{j}](\mathbf{r}-\mathbf{x}(t),t) \tag{2.105}$$

$$\mathbf{A}_{xc}[\mathbf{j}'](\mathbf{r},t) = \mathbf{A}_{xc}[\mathbf{j}](\mathbf{r}-\mathbf{x}(t),t), \tag{2.106}$$

where

$$\mathbf{j}'(\mathbf{r},t) = \mathbf{j}(\mathbf{r}-\mathbf{x}(t),t) + \frac{\partial \mathbf{x}(t)}{\partial t}\rho(\mathbf{r}-\mathbf{x}(t),t), \tag{2.107}$$

with $\mathbf{x}(t)$ an arbitrary time-dependent function. The above equations simply state that a rigid translation of the current density implies the same rigid translation of the exchange-correlation potentials. The rigid translation of the current density implies a rigid translation of the density according to $\rho'(\mathbf{r},t) = \rho(\mathbf{r}-\mathbf{x}(t),t)$ through the continuity equation. Note that if $\mathbf{x}(t) = \mathbf{u}t$ the above equations guarantee that the exchange-correlation potentials satisfy Galileian invariance. In TDDFT where we consider time-dependent external fields that can be described by solely scalar potentials the above equations reduce to [42]

$$v_{xc}[\rho'](\mathbf{r},t) = v_{xc}[\rho](\mathbf{r}-\mathbf{x}(t),t), \tag{2.108}$$

where $\rho'(\mathbf{r},t) = \rho(\mathbf{r}-\mathbf{x}(t),t)$.

It is easy to see that the ALDA exchange-correlation potential given in Eq. (2.26) satisfies the generalized translation invariance (2.108). We will now show that the ALDA exchange-correlation potential also satisfies the zero-force and zero-torque the-

orems. The exchange-correlation force and torque are then given by

$$\mathbf{F}_{xc}^{ALDA}(\mathbf{r},t) = \int d\mathbf{r}\rho(\mathbf{r},t)\nabla\left\{\left.\frac{d\epsilon_{xc}(\rho)}{d\rho}\right|_{\rho=\rho(\mathbf{r},t)}\right\} \tag{2.109}$$

$$\mathbf{T}_{xc}^{ALDA}(\mathbf{r},t) = \sum_{ijk}\mathbf{e}_i\epsilon_{ijk}\int d\mathbf{r}\rho(\mathbf{r},t)r_j\partial_k\left\{\left.\frac{d\epsilon_{xc}(\rho)}{d\rho}\right|_{\rho=\rho(\mathbf{r},t)}\right\}, \tag{2.110}$$

where ϵ_{ijk} is the Levi-Civita antisymmetric tensor. Performing an integration by parts we obtain

$$\mathbf{F}_{xc}^{ALDA}(\mathbf{r},t) = -\int d\mathbf{r}[\nabla\rho(\mathbf{r},t)]\left.\frac{d\epsilon_{xc}(\rho)}{d\rho}\right|_{\rho=\rho(\mathbf{r},t)} \tag{2.111}$$

$$= -\int d\mathbf{r}\nabla\left\{\epsilon_{xc}(\rho)|_{\rho=\rho(\mathbf{r},t)}\right\} = 0 \tag{2.112}$$

$$\mathbf{T}_{xc}^{ALDA}(\mathbf{r},t) = -\sum_{ijk}\mathbf{e}_i\epsilon_{ijk}\int d\mathbf{r}\left\{\partial_k[r_j\rho(\mathbf{r},t)]\right\}\left.\frac{d\epsilon_{xc}(\rho)}{d\rho}\right|_{\rho=\rho(\mathbf{r},t)} \tag{2.113}$$

$$= -\sum_{ijk}\mathbf{e}_i\epsilon_{ijk}\int d\mathbf{r}r_j\left\{\partial_k[\rho(\mathbf{r},t)]\right\}\left.\frac{d\epsilon_{xc}(\rho)}{d\rho}\right|_{\rho=\rho(\mathbf{r},t)} \tag{2.114}$$

$$= -\sum_{ijk}\mathbf{e}_i\epsilon_{ijk}\int d\mathbf{r}\partial_k\left\{r_j\epsilon_{xc}(\rho)|_{\rho=\rho(\mathbf{r},t)}\right\} = 0, \tag{2.115}$$

where Eqs. (2.112) and (2.115) vanish due to Gauss' theorem.